Condensed Matter Science

Dynamics and Phase Transitions

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Infrared conductivity of photocarriers in organic molecular crystals

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This project, begun in March of 2001, seeks use infrared spectroscopy to probe the properties of photocarriers in organic molecular crystals. A group at Bell Laboratories has recently succeeded in creating FETs on ultrapure single crystals of pentacene, tetracene, and other "polyacenes" (rigid, rodlike chains of Benzene rings). Carriers injected into these transistors have exhibited metal-insulator transitions, superconductivity, lasing, and the quantum Hall effect (see, e.g., J. H. Schoen, Ch. Kloc, B. Batlogg, *Science* v. 288 p. 2338; *Science* v. 288 p. 656; *Nature* v. 406 p. 702). The goal of our experiment is to photoexcite carriers in these same materials, and to measure the infrared spectrum of these photocarriers.

The apparatus, at ALS beamline 1.4, includes an Argon-ion laser for photoexcitation of charge carriers, a Bruker 66v/S Fourrier-Transform Infrared (FTIR) spectrometer, and a variable-temperature cryostat. The laser allows photoexcitation at energies from 2.4 eV to 3.5 eV. At the UV frequencies, the quantum efficiency of photocarrier generation in pentacene is high, about 30%. The light is coupled to the sample (in the cryostat) by means of an optical fiber. The cryostat allows us to reach temperatures from 5 K to 300 K, and the FTIR spectrometer allows measurement of infrared transmission on the range of at least 100 cm^{-1} to 7800 cm^{-1}.

The basic result of a measurement is a transmission spectrum, $T(\omega)$, either with the sample illuminated with laser light, $T_{on}(\omega)$, or with the sample unilluminared, $T_{off}(\omega)$. From these spectra we determine difference spectra, $\Delta T / T = (T_{on}(\omega) - T_{off}(\omega)) / T_{off}(\omega)$. Our measurements at room temperature on crystals of Tetracene have shown good reproducibility, both in the shape and in the magnitude of the difference spectra. The measurement is sensitive to changes in the transmission of one part in 10^4 or better through most of the spectral range. We have resolved many clear and reproducible features that are an order of magnitude larger than the noise.

Although these results demonstrate that the apparatus is, indeed, able to make the desired measurements, they do not put us particularly close to our scientific goals. Most or all of the features we have seen thus far appear to be due to shifting or broadening of phonon absorptions due to the heating effect of the laser. This result at room temperature is no surprise, as the mobility of carriers in polyacene crystals increases as T^{-2} below room temperature, so that the conduction of the carriers should only become visible at low temperatures. More surprising was the result that tetracene crystals large enough to measure optically will invariably shatter upon cooling below about 180 K (the temperature seems to vary a bit). Pentacene crystals, on the other hand, do not shatter, but also do not seem to be available in sizes large enough for optical measurement. Other

polyacenes have much lower efficiencies of photocarrier generation (due to their having broader bandgaps), and so are not suited to this experiment.

We are now seeking thin-film samples of the polyacenes, as these should survive cooling and should have the large area desirable for infrared measurement. High-quality pentacene films have been shown to display many of the same electronic properties as their single-crystal counterparts (J. H. Schoen, Ch. Kloc, *Applied Physics Letters*, v. 79, p. 4043).

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X-ray spectromicroscopy of branched polyolefin blends

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INTRODUCTION

It is generally difficult to determine the phase diagram of polyolefin blends directly by measuring the composition of phase separated domains. The constituent materials differ only in the amount and/or length of sidechains and provide little spectroscopic differences and limited contrast in traditional miroscopies [1-3]. Indirect methods to determine the phase diagram involve a large number of samples and elaborate contrast enhancement methods. Here, we explore the utility of Near Edge X-ray Absorption Fine Structure (NEXAFS) microscopy to determine polyolefin phase diagrams directly by determining the composition of phases in a limited number of samples. We have used the scanning transmission X-ray microscope (STXM) at beamline 7.0 to investigate thermally annealed blends of an ethylene-butene copolymer (EBC with 3.7 mol % butene) and of an ethylene-octene copolymer (EOC with 3.33 mol % octene). Despite the very similar chemical structure of these copolymers (they differ only in the length of the side chain, i.e. ethyl versus hexyl groups) NEXAFS microscopy can be used to a) directly visualize the morphology without staining or etching, and b) determine the composition of the phases in such blends.

EXPERIMENTAL

0.1 % m/m solutions of EBC and EOC (experimental polymer made with single site catalyst technology) in xylene were mixed in two different ratios (samples A1-4: 33%, samples C1-4 67% EOC). Subsequently, methanol was added to precipitate the polymer. The precipitate was collected by filtering and dried. The samples were vacuum-annealed at 180°C (samples A1, C1), 160°C (samples A2, C2), 140°C (samples A3, C3) and 120°C (samples A4, C4), respectively, quenched to -7°C and cryo-microtomed to about 100-200 nm in thickness.

The data were acquired at beamline 7.0.1. C1s-NEXAFS reference spectra of the pure components were derived from line-spectra (i.e. the same line scan at many photon energies). Image sequences of up to 80 images of small areas (typically 10 μm x 10 μm) as well as small series of large images (typically 6 images, 60 μm x 60 μm) were also recorded.

RESULTS AND DISCUSSION

The C1s-NEXAFS spectra of the two components are shown in Fig. 1. The most noticeable difference between both spectra is found in the 287-288eV energy region. EBC shows two closely spaced peaks (typical for linear polyethylene or polyolefins with few or short side-chains), EOC shows only one broad signal (typical for polyolefins with many or long side-chains). These signals are interpreted as $\sigma^*(C-H)$ resonances [4]. Their spectral variations primarily reflect different intermolecular distances rather than different degrees of crystallinity. These spectra were used as reference spectra during the "stack fit" procedure [5] to determine the component maps.

Fig. 2 shows typical optical density (OD) images of two of the samples. The domains of the two phases can be clearly distinguished. Because EBC shows a higher absorption coefficient at 288.2eV than EOC (see Fig. 1), regions with high EBC concentration appear bright in Fig. 2b
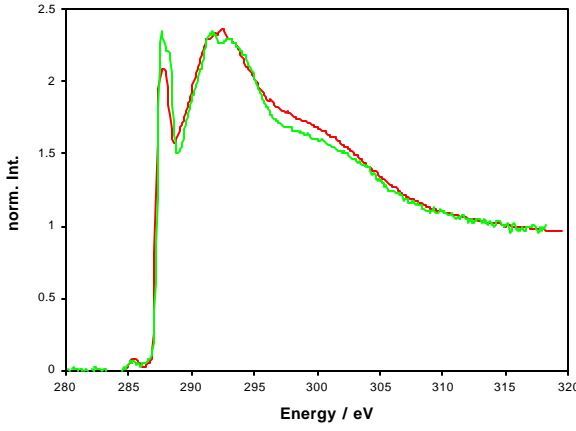
Fig. 1: C1s-NEXAFS reference spectra of the components: Red: ethylene-octene copolymer, green: ethylene-butene copolymer, both normalized to an edge jump of unity between 283eV and 315eV.

Fig. 2: Typical STXM optical density (OD) images of samples A3 (33% ethylene-octene copolymer): a), b) and C3 (67% ethylene-octene copolymer): c), d). Images a) and c) are taken at 287.1eV. Here domains, which are rich in the ethylene-octene copolymer appear bright. Images b) and d) are taken at 288.2eV and ethylene-butene rich domains appear bright in this case.

and 2d. At 287.1eV the opposite is the case and EOC rich regions appear bright. As expected from the ratio of the components in the mixed solutions, EBC forms the matrix- or majority-phase in sample A3 (a,b) and EOC in sample C3 (c,d).

After the images of an images sequence are aligned to correct for lateral shifts, the spectrum of each pixel in the stack area can be fitted by a linear combination of the reference spectra ($R_{oct}(E)$ and $R_{but}(E)$) and a constant, which is energy-independent (*constant*):

$$OD(E, x, y) = t_{oct}(x,y)*R_{oct}(E) + t_{but}(x,y)*R_{but}(E) + constant(x,y)$$

Thereby matrices of the effective thickness of the components $t_{oct}(x,y)$ and $t_{but}(x,y)$ and of the constant are determined and can be represented by component maps.

From these maps, regions in the matrix and in the minority phase were chosen carefully to not include inclusions of the other phase. Averaging over all pixels of these regions yields the effective thicknesses t. Since the sample contained only the two polymers, the composition Φ_{oct} (here the mass-fraction of EOC) can be calculated:

$$\Phi_{oct} = \frac{t_{oct}}{t_{oct}+t_{but}}$$

Thus, two composition values, one for the matrix and one for the minority phase, are derived for each sample. Fig. 3 shows these results for the different annealing temperatures. If we assume that the thermodynamical equilibrium was reached during the annealing and that the quenching conserved the composition of the melt, this diagram can be interpreted as a phase diagram. Although we presently estimate large errors (10-15%), an upper critical solution temperature behavior and a broad two-phase region is clearly visible.
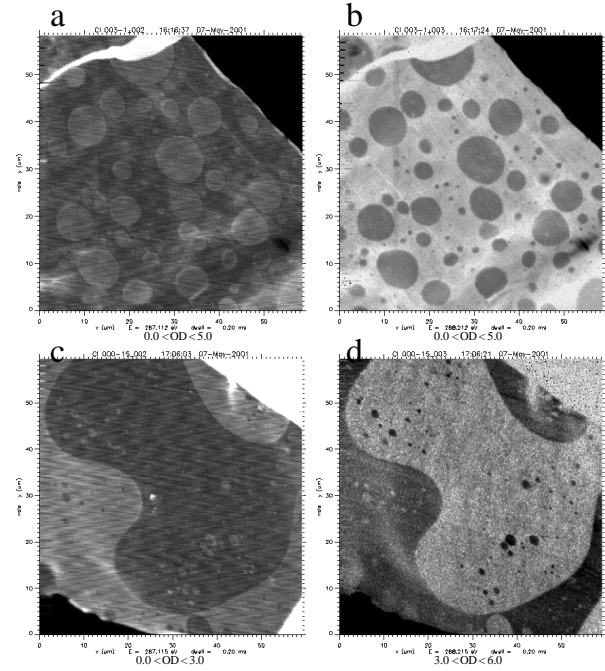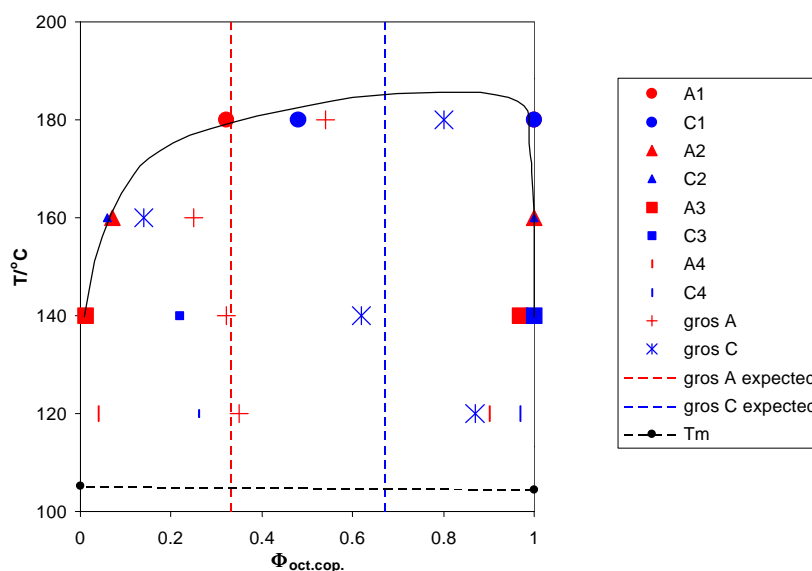
Fig. 3: Proposed phase diagram for the system poly(ethylene-ran-butene) – poly(ethylene-ran-octene). Small symbols were used, if the estimated reliability of the data was low. The gross amounts of the components from area weighted averages of the compositions and the gross amount expected from the preparation are indicated also.

In summary, we used NEXAFS-microscopy to determine the morphology and the composition of a specific polyolefin blend. The differences in the NEXAFS spectra of short- and long-branch copolymers provide sufficient image contrast, especially in the 287-288eV energy region, to image the morphology without further sample preparation (staining, etching). The polymers investigated show phase separation at all annealing temperatures. The matrix phase is always formed by the component that had the higher concentration in the solution and in the case of the EBC rich samples the gross sample composition is close to the solution composition. This indicates an almost quantitative precipitation by methanol. The phase diagram can be determined by quantitative evaluation of image sequences.

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